— Headline —

Electrochemical and Spectroelectrochemical Studies on Sandwich-type Bis(phthalocyaninato)lanthanide Complexes

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Sandwich-type bis(phthalocyaninato)lanthanide complexes, $[\text{Ln}(\text{Pc})_2]^z$, exhibit intriguing characteristics which stem from the interactions between the two π -conjugated phthalocyanine rings held by the central metal ion in close proximity, and they have been explored as materials for electrochromic displays, molecular semiconductors, gas-sensors and for nonlinear optical applications. This article reviews some topics on their structural, electrochemical, chemical, and spectral characteristics.

Key Words : Phthalocyanine, Double-decker Complex, Spectroelectrochemistry

1 Introduction

Bis(phthalocyaninato)lanthanide complexes, $[\text{Ln}(\text{Pc})_2]^z$ (where Ln is a lanthanide, Pc^{2-} is phthalocyanine dianion ($\text{C}_{32}\text{N}_8\text{H}_{16}$), and z is the charge), have attracted much attention because of their electrochromic property. Since the first report by Moskalev and Kirin¹⁾ of electrochromic behavior of a solid film of a bis(phthalocyaninato)lanthanide on a tin oxide substrate, much work has been carried out with a view to applying these complexes to electrochromic displays.²⁾ They are also considered as materials for molecular semiconductors,^{3,4)} as attractive candidates for nonlinear optical applications,⁵⁾ and as materials for gas-sensors.^{6,7)} Besides such application-oriented researches, considerable efforts have been made to investigate their spectral,^{8–10)} electrochemical,^{11–13)} magnetic,^{14,15)} and structural^{16–18)} properties. Theoretical approaches to the electronic states of the complexes have also been attempted.^{19–22)} Most of the intriguing properties of the bis(phthalocyaninato)lanthanide complexes stem from their sandwich-type structure and the interaction between the π -conjugated systems of the Pc rings held in close proximity. By using a series of lanthanide ions, the distance between the Pc rings can be changed and the effect of the distance on various properties can be explored. Beside lanthanides, such sandwich-type complexes have also been obtained for metal ions of large size, e.g., actinides such as $\text{U}^{23)}$ and $\text{Th}^{24)}$ and group 4 transition metals such as $\text{Ti}^{25)}$ $\text{Sn}^{26)}$ and $\text{Zr}^{27)}$

Though the bis(phthalocyaninato) complexes have

been the subjects of researches over the past three decades, their structures and electronic states have not been clarified completely. In the work at earlier stage before the middle of the eighties, the complexes under study were not always identified, which often caused misunderstandings of the experimental results. One of the main reasons for the difficulty in the identification of the complexes is the fact that the synthesized crude products are always mixtures of different complexes and thus separation and purification of the complexes by chromatography on alumina or silica columns and/or vacuum sublimation are required. Large molecular weights of the complexes also make it difficult for us to identify them by elemental analysis and by mass spectroscopy.

In this article, we review some of the topics on the characteristics of bis(phthalocyaninato)lanthanides and describe what have been clarified through our recent studies.

2 Synthesis of the Complexes

Bis(phthalocyaninato)lanthanides were synthesized from a mixture of lanthanide(III) acetate (or chloride), *o*-dicyanobenzene and Na_2CO_3 according to the method of Moskalev and Kirin²⁸⁾ with several important modifications, one of which was the programmed control of the reaction temperature. Though the detailed procedure was described elsewhere,²⁹⁾ it is noteworthy that the product complexes were collected as the tetrabutylammonium salts, $[\text{N}(\text{C}_4\text{H}_9)_4]^+ [\text{Ln}(\text{Pc})_2]^-$. The crude product is usually a mixture of components that give a blue solution and a green

solution, together with other impurities such as metal-free phthalocyanine and, in certain cases, triple-decker complexes. At present, the blue component is believed to be a salt of $[\text{Ln}(\text{Pc})_2]^-$ and the green one is a neutral species $[\text{Ln}(\text{Pc})_2]^0$ which is formed from the oxidation of $[\text{Ln}(\text{Pc})_2]^-$ by dioxygen. There remains, however, some uncertainty and controversy concerning of the "green component"; besides the neutral complex $[\text{Ln}(\text{Pc})_2]^0$, a protonated complex $\text{H}[\text{Ln}(\text{Pc}^{2-})_2]$ has been proposed.³⁰ It is almost impossible to determine by elemental analysis whether a proton is present or not. It is much more reliable to identify the product as $[\text{N}(\text{C}_4\text{H}_9)_4]^+[\text{Ln}(\text{Pc})_2]^-$ by elemental analysis, and then further identification by spectroscopic methods becomes significant. We have synthesized the complexes for thirteen lanthanide metals: $\text{Ln}=\text{La}$, Pr , Nd , Sm , Eu , Gd , Tb , Dy , Ho , Er , Tm , Yb , and Lu .

3 Crystal and Molecular Structures of $[\text{N}(\text{C}_4\text{H}_9)_4]^+[\text{Ln}^{\text{III}}(\text{Pc})_2]^-$ ($\text{Ln}=\text{Nd}$, Gd , Ho , Lu)

Extensive studies on the structures of lutetium complexes have been carried out by Weiss and co-workers^{17,18}) and several structures of the $[\text{Ln}^{\text{III}}(\text{Pc})_2]$ complexes have been reported.³¹⁻³³) As shown in Fig. 1, the lanthanide ion occupies the central position with eight coordinated nitrogen atoms of the two Pc rings which are parallel and are somewhat domed. It has been generally accepted the Pc rings are in a staggered conformation relative to each other (approximately 45°).

Single crystals for the four title complexes $[\text{N}(\text{C}_4\text{H}_9)_4]^+[\text{Nd}(\text{Pc})_2]^-$, $[\text{N}(\text{C}_4\text{H}_9)_4]^+[\text{Gd}(\text{Pc})_2]^-$, $[\text{N}(\text{C}_4\text{H}_9)_4]^+[\text{Ho}(\text{Pc})_2]^- \cdot \text{H}_2\text{O}$, $[\text{N}(\text{C}_4\text{H}_9)_4]^+[\text{Lu}(\text{Pc})_2]^- \cdot \text{H}_2\text{O}$ could be obtained and their crystal and molecu-

lar structures were analyzed by X-ray crystallography.²⁹) In all the crystals, the $[\text{Ln}(\text{Pc})_2]^-$ and $[\text{N}(\text{C}_4\text{H}_9)_4]^+$ ions stack alternately along the 4-fold axes. The projection of the Nd complex viewed along the diagonal axis in the ab plane is shown in Fig. 2 in order to show the packing mode. The central lanthanide ions are 8-fold coordinated by the isoindole nitrogen atoms, N_{iso} , of the Pc rings that form a saucer shape. Crystal structures of the other three complexes are similar to the Nd complex. Figure 3 shows the ORTEP drawings of the molecular structures of the four complexes viewed along the 4-fold axis. This figure clearly exhibits that the four molecules are similar to each other except for the skew angle of the two Pc rings; the calculated skew angles are also indicated in Fig. 3.

The plane composed of four N_{iso} atoms of the Pc ring is at a right angle to the 4-fold axis. It was found that the interplanar distance, d_{N} , that is defined as the distance between the two upper and lower planes composed of four N_{iso} atoms, linearly dependent on the ionic radius, as shown in Fig. 4. There seems no relationship between the skew angle and d_{N} , though the skew angle seems to depend on the strength of the $\pi-\pi$ interaction between the two Pc rings. This may be due to the fact that the d_{N} values are too small considering the van der Waals radius of the aromatic carbon atom. We define the $\pi-\pi$ interaction distance, d_{int} , as the distance between the average planes of the upper and lower Pc rings. Figure 5 plots the skew

Fig. 1 Molecular structure of $[\text{Ln}^{\text{III}}(\text{Pc})_2]^-$ ion.

Fig. 2 Crystal structure of $[\text{Nd}^{\text{III}}(\text{Pc})_2]^-$ viewed along $[110]$. The disordered $[\text{N}(\text{C}_4\text{H}_9)_4]^+$ ions are sandwiched between the $[\text{Nd}^{\text{III}}(\text{Pc})_2]^-$ ions.

Fig. 3 Molecular structures of $[\text{Ln}^{\text{III}}(\text{Pc})_2]^-$. $\text{Ln}=\text{Nd}$ (a), Gd (b), Ho (c) and Lu (d).

Fig. 4 Plots of the interplanar distances, d_{π} , against the ionic radii of the central atoms. The black squares indicate the four $[\text{Ln}^{\text{III}}(\text{Pc})_2]^-$ ions in Fig. 3.

Fig. 5 Plots of the skew angles against the π - π interaction distances, d_{int} . The black squares indicate the four $[\text{Ln}^{\text{III}}(\text{Pc})_2]^-$ ions in Fig. 3, and the black triangles are plots of the MPc complexes.

angle against d_{int} . As d_{int} value increases, the skew angle gradually decreases almost linearly. The linear relationship is changed when d_{int} value is greater than 3.5, which is the sum of the van der Waals radii of the aromatic carbon atoms. This may suggest that as the π - π interaction decreases, the skew angle decreases and approaches zero if the π - π interaction becomes sufficiently small. We may expect that the La complex would have the skew angle close to zero because La^{III} ion has the largest ionic radius among lanthanides. We noticed recently that the crystal structure of $[\text{La}(\text{Pc})_2]^0 \cdot \text{CH}_2\text{Cl}_2$ was determined by Ostedorp and Homborg;³⁴⁾ they obtained the skew angle value of 45° in spite of our expectation. Though the primary difference from ours is that the La complex is a neutral species, we cannot give any explanation at present about this discrepancy in the structure. Further preparation of single crystals for a series of the lanthanide complexes, $[\text{Ln}(\text{Pc})_2]^-$ and $[\text{Ln}(\text{Pc})_2]^0$, and the determination of their structures will be required.

4 Electrochemical Characteristics of $[\text{Ln}(\text{Pc})_2]^z$

The cyclic voltammograms of $[\text{N}(\text{C}_4\text{H}_9)_4]^+ [\text{Ln}(\text{Pc})_2]^-$ in *o*-dichlorobenzene solutions at a gold microelectrode are shown in Fig. 6 for the five complexes.¹³⁾ All the complexes exhibit three one-electron reduction waves and three one-electron oxidation waves, corresponding to

and

respectively. Processes (1), (2), (4) and (5) are almost reversible (k^0 values were found to lie in the range 2.1 – 2.5×10^{-2} cm/s from the faradaic impedance measurements) and they are considered as the redox processes occurring at the Pc moiety, as shown in the next section. On the other hand, step (3) is quasi-reversible and step (6) is accompanied by adsorption of the product and appears as an irreversible one. Processes (3) and (6) are very sensitive to the solvents and electrode materials; they were observed by using the combination of dichlorobenzene and a gold electrode for the first time. The values of formal potentials E^0 's for steps (4) and (5), $E^0_{(4)}$ and $E^0_{(5)}$, are almost linearly dependent on the ionic radius of the central metal and become less positive as the ionic radius decreases. This tendency can be explained as follows; the smaller the interplanar distance, the more increased the overlap integrals of MO's, resulting in the lift-up of the HOMO of $[\text{Ln}(\text{Pc})_2]^-$ so that the less energy is required to remove the first two electrons from the complex. On the other hand, $E^0_{(1)}$ and $E^0_{(2)}$ are less sensitive to the ionic radius than $E^0_{(4)}$ and

Fig. 6 Cyclic voltammograms for reduction (left) and oxidation (right) of 0.5 mmol/dm^3 $[\text{Ln}(\text{Pc})_2]^-$ in *o*-dichlorobenzene containing 0.2 mol/dm^3 tetrabutylammonium perchlorate at a gold microdisk electrode of $25 \mu\text{m}$ in diameter. Sweep rate was 0.1 V/s .

$E_{(5)}^{0'}$, which is considered as the result of the weaker interaction of the LUMO's of the two Pc moieties.

The green form of the complex $[\text{Ln}^{\text{III}}(\text{Pc})_2]^0$ is now considered as a neutral radical species. Though it may be expressed as $[\text{Ln}^{\text{III}}(\text{Pc}^{2-})(\text{Pc}^{\cdot-})]^0$, the hole on $(\text{Pc}^{\cdot-})$ is not localized on one of the Pc rings but is delocalized over the two Pc rings. However, the possibility of equilibrium of the radical form with the complex of the quadrivalent metal ion, $[(\text{Pc}^{2-})\text{Ln}^{\text{IV}}(\text{Pc}^{2-})]^0$, has been proposed.³⁶⁾ This possibility will be discussed in section 7.

5 Electronic Absorption Spectra of $[\text{Ln}(\text{Pc})_2]^z$

Electrochemical measurements described in the previous section revealed that $[\text{Ln}(\text{Pc})_2]^z$ has seven different oxidation states from $z = -4$ to 2. Studies on the electronic spectra of these complexes have been carried out extensively in connection with electrochromic displays and they have been reviewed.²⁾ Chang and Marchon⁹⁾ were the first who proposed the following scheme for the color changes in solution accompanied by the redox processes for the Lu complex:

and this scheme is now generally accepted. UV/visible absorption spectra of $[\text{Ln}(\text{Pc})_2]^z$ for different oxidation states were obtained by use of spectroelectrochemical cells under potentiostatic control. An example of such spectra recorded at various potentials is shown in Fig. 9 in section 6. Isosbestic points are clearly seen in the spectra, indicating that a chemically reversible interconversion between different oxidation states ($z = -1$ and 0) takes place. Such reversible interconversions were observed for processes (1), (2) and (4). For process (5), however, isosbestic points could not be observed except for Lu and Yb complexes due to the decrease in the solubility of the $[\text{Ln}(\text{Pc})_2]^+$ and their adsorption to the electrode. Absorption spectra for $[\text{Ln}(\text{Pc})_2]^z$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Gd}, \text{Yb}, \text{and Lu}$, and $z = 3-, 2-, 1-, 0$ and $1+$) are shown in Fig. 7. It is clearly seen from Fig. 7 that the spectra change systematically as the radius of the central metal decreases. The electronic absorption spectra of phthalocyanine complexes are characterized by the Q band in the range from 600 to 700 nm and the B band (Soret band) around 330 nm. The Q band is assigned to the $\pi\text{-}\pi^*$ transition ($a_{1u} \rightarrow e_g$) and the B band is attributed to the transitions from a_{2u} and b_{2u} to e_g . The increased splitting of the Q band observed for $[\text{Ln}(\text{Pc})_2]^-$ when the radius of the metal ion decreases has been explained by the strong interaction of HOMO's of the two Pc rings. It is interesting to note that the reduced forms, $[\text{Ln}(\text{Pc})_2]^{2-}$ and $[\text{Ln}(\text{Pc})_2]^{3-}$, having one and two electrons in the LUMO, respectively, exhibit a splitting of absorption

Fig. 7 Comparison between the electronic spectra of $[\text{Ln}(\text{Pc})_2]^z$ ($\text{Ln} = \text{Lu}, \text{Yb}, \text{Gd}, \text{Nd}$ and La). $z = -3$ (a), -2 (b), -1 (c), 0 (d) and $+1$ (e).

band around 600 nm and the degree of the splitting increases as the radius of the central ion increases (see Fig. 7 (a), (b)). This behavior has not been treated theoretically.

Figure 8 (a) compares the spectra of $[\text{Lu}(\text{Pc})_2]^+$ and $[\text{Lu}(\text{Pc})_2]^{2+}$, which are recorded at +1.0 V and +2.1 V, respectively. These spectra are quite similar to each other, suggesting that the oxidized moiety in process (6) may not be the Pc ring, but the central metal as expressed by

Similarly, Fig. 8 (b) shows that the spectrum of $[\text{Lu}(\text{Pc})_2]^{3-}$ is very close to that of $[\text{Lu}(\text{Pc})_2]^{4-}$, suggesting that it is not the Pc ring but the lutetium ion that may be reduced in process (3) as described by

However, $[\text{Lu}^{\text{III}}(\text{Pc}^{3-})_2]^{3-}$ and $[\text{Lu}^{\text{II}}(\text{Pc}^{3-})_2]^{4-}$ are oxidized very easily by dioxygen, and the possibility of continued oxidation of $[\text{Lu}^{\text{II}}(\text{Pc})_2]^{4-}$ by a trace of oxygen present in the solution cannot be ruled out. We think that a further study is necessary to confirm this postulated mechanism.

Fig. 8 (a) Absorption spectra of [Lu(Pc)₂]⁺ (solid curve: +1.0 V) and [Lu(Pc)₂]²⁺ (dashed curve: +2.1 V). (b) Absorption spectra of [Lu(Pc)₂]³⁻ (solid curve: -1.6 V) and [Lu(Pc)₂]⁴⁻ (dashed curve: -2.1 V).

6 Reactions of Bis(phthalocyaninato)-lanthanide Complexes with Acids and Bases

Daniels *et al.*^{36,37} reported that when acid such as trifluoroacetic acid was added to the blue solution of bis(phthalocyaninato)lanthanide, the color of the solution changed to green and/or red, and that the addition of triethylamine to the resulting solution give rise to a blue solution again. They claimed that the color change was not due to oxidation-reduction reaction but due to acid-base reaction as expressed by

However, this mechanism was ruled out by our results described below.

Figure 9 compares the spectral change of the blue solution in *o*-dichlorobenzene when the solution was electrochemically oxidized in a thin-layer spectroelectrochemical cell at various potentials between 0.0 V and 0.3 V vs. AgCl/Ag and that of the [Lu(Pc)₂]⁻ solution in *o*-dichlorobenzene when acetic acid was added stepwise. The two spectra completely agree in shape to each other, indicating that the same species are formed in both solutions.

Figure 10 shows cyclic voltammograms for (1) the [Lu(Pc)₂]⁻ solution, (2) [Lu(Pc)₂]⁰ solution generated by electrooxidation of [Lu(Pc)₂]⁻, (3) a mixture of [Lu(Pc)₂]⁻ solution and acetic acid, and (4) a mixture of [Lu(Pc)₂]⁰ solution and triethylamine. Curve (3) is the same as (2), indicating that [Lu(Pc)₂]⁰ is formed when acetic acid was added to [Lu(Pc)₂]⁻. Curve (4) indicates that [Lu(Pc)₂]⁻ is formed by the addition of triethylamine to [Lu(Pc)₂]⁰ solution. Furthermore, the increase in the anodic current at 0.6 V and some distortion of the curve at the negative potential region. From these results together with detailed comparisons of the kinetics of reaction of [Lu(Pc)₂]⁻ and acids in the absence and the presence of oxygen, we concluded that the color change from blue to green was caused by acid-catalyzed oxidation of [Lu(Pc)₂]⁻ by molecular dioxygen. The reaction mechanism is expressed by

Fig. 9 (a) Thin-layer absorption spectra of 0.2 mmol/dm³ [Lu(Pc)₂]⁻ when it was oxidized at various potentials, and (b) variation of absorption spectra of 0.01 mmol/dm³ [Lu(Pc)₂]⁻ in *o*-dichlorobenzene with addition of acetic acid.

Fig. 10 Cyclic voltammograms of 0.4 mmol/dm³ [Lu(Pc)₂]⁻ and [Lu(Pc)₂]⁰ and their mixtures with acetic acid (AcH) and triethylamine (TEA), respectively, at a gold microdisk electrode of 25 μm in diameter. Sweep rate was 100 mV s⁻¹.

HO₂ radical formed as an intermediate is an oxidizing agent strong enough to oxidize the green [Lu(Pc)₂]⁰

solution to the reddish $[\text{Lu}(\text{Pc})_2]^+$. Furthermore, we have confirmed that triethylamine serves as a reducing agent from the catalytic current observed for the oxidation of $[\text{Lu}(\text{Pc})_2]^-$ in the presence of triethylamine. The mechanism is given as follows:

Thus, the acid-base reaction mechanism given by Eq. (7) was ruled out.

7 ESR Measurements and Oxidation States of $[\text{Ln}(\text{Pc})_2]^0$

Since Corker and coworkers³⁹⁾ found that the green form of bis(phthalocyaninato)lutetium shows an ESR signal corresponding to an organic radical as shown in Fig. 11, attention was focused on the identification of the green form and at present it is almost recognized that the green species is not $[\text{Ln}(\text{Pc})_2]\text{H}$ but a neutral radical $[\text{Lu}(\text{Pc})_2]^0$ as mentioned in section 4. This is paramagnetic and an unpaired electron is considered to be delocalized over the two Pc rings. No ESR signals, however, have been reported for $[\text{Ln}(\text{Pc})_2]^0$ other than Lu, except for the only paper by Kasuga and coworkers.³⁹⁾ They claimed that they observed ESR signals of organic radicals of bis(phthalocyaninato) complexes of La^{III} , Nd^{III} and Y^{III} . However, they used *p*-benzoquinone as an oxidizing agent and thus it seems reasonable to consider that the origin of the ESR signals they observed was not the bis(phthalocyaninato) complexes but semiquinone formed from benzoquinone. Based on the fact that no ESR signal has been reported except for the Lu complexes, Tomilova *et al.*³⁵⁾ proposed that central ion is oxidized by way of the intramolecular ligand-to-metal charge transfer to form $[(\text{Pc}^{2-})\text{Ln}^{\text{IV}}(\text{Pc}^{2-})]^0$.

However, the systematic variations of the Q band and the B bands in the electronic absorption spectra of $[\text{Ln}(\text{Pc})_2]^0$ were observed when the central metal ion was changed from La to Lu (see Fig. 7(d)). This fact clearly suggests the presence of the form $[(\text{Pc}^{2-})$

$\text{Ln}^{\text{III}}(\text{Pc}^{2-})]^0$. Therefore, we carried out ESR measurements of *o*-dichlorobenzene solutions of $[\text{Ln}(\text{Pc})_2]^0$ (green) and $[\text{Ln}(\text{Pc})_2]^-$ (blue) complexes for several lanthanides. Though they did not exhibit any responses at ambient temperatures, we could observe the ESR response at -150°C for $[\text{Eu}(\text{Pc})_2]^0$, $[\text{Sm}(\text{Pc})_2]^0$, $[\text{Gd}(\text{Pc})_2]^0$ and $[\text{Gd}(\text{Pc})_2]^-$. Though the shapes of the spectra for $[\text{Sm}(\text{Pc})_2]^0$, $[\text{Gd}(\text{Pc})_2]^0$ and $[\text{Gd}(\text{Pc})_2]^-$ are involved and cannot be interpreted at present, $[\text{Eu}(\text{Pc})_2]^0$ showed the well-defined ESR signals at $g=2.007$ as shown in Fig. 12, indicating the presence of an organic free radical. The ESR signal showed temperature dependence and the signal intensity decreased when temperature increased and at about -70°C , the signal disappeared. It should be noted that even though the lanthanides(III) from Ce to Yb are paramagnetic because of 4 f electron(s), none but $[\text{Gd}(\text{Pc})_2]^-$ show any ESR response. It is interesting to note that we could observe ESR responses of the radical species only for Sm^{III} , Eu^{III} and Gd^{III} , all of which have small values of effective magnetron, μ_{eff} . Especially, $\mu_{\text{eff}}=0$ for Eu^{III} . These results seem to indicate that strong interactions between the p-radical and 4 f electrons of lanthanide ions are usually present so that the intensity of the ESR signals may be reduced to zero. Only when the effective magnetron value is small, the ESR signal from the radical becomes observable at low temperatures, though the signal intensity is weak.

8 Concluding Remarks

The characteristics of the bis(phthalocyaninato) complexes discussed in this article were very limited. Though we have not mentioned any results from various spectroscopic methods such as IR and Raman spectroscopy, ^1H NMR, and mass spectroscopy, they are now extensively used for the identification and the characterization of the complexes. Accumulations of data from the systematic studies will be required for the better understanding of these complexes.

Among various sandwich-type complexes, so-called heteroleptic complexes, which have different macrocycles like phthalocyanine and porphyrin, have

Fig. 11 ESR spectrum of $[\text{Lu}(\text{Pc})_2]^0$ in *o*-dichlorobenzene at room temperature.

Fig. 12 ESR spectra of $[\text{Eu}(\text{Pc})_2]^0$ in *o*-dichlorobenzene at several low temperatures.

been studied over the past decade and the developments in the field have been summarized in a recent review by Ng and Jiang.⁴⁰⁾ Comparison of the data for homoleptic and heteroleptic complexes will help us to gain more profound insight into the characteristics of these complexes.

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